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Effect of illumination on the crystallization kinetics of amorphous $Se_{80-x}Te_{20}In_x$

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The present paper reports the effect of illumination on the crystallization kinetics in amorphous $Se_{80-x}Te_{20}In_x$ ($0 \leqslant x \leqslant 10$). The crystallization was monitored by measuring the electrical conductivity of isothermally annealed samples held at temperatures near the crystallization temperature. It is observed that the crystallization becomes faster in the presence of light as compared to a pure thermal case. There is no significant change in the activation energy under illuminated conditions as compared to the purely thermal case.

1. Introduction

It is well established that photocrystallization occurs in both selenium and selenium based chalcogenide glasses [1–6]. Kotkata *et al.* [7, 8] have studied the effect on crystallization kinetics of shining light on amorphous selenium that had been doped with sulpher and showed that the illumination opposes the crystal growth. Matsushita *et al.* [9] have also reported that crystallization is suppressed on the illumination of a-Ge_xSe_{1-x} ($0 \leqslant x < 0.2$) films for $x > 0.05$. However, for $Ge_{0.05}Se_{0.95}$ films, the crystallization was found to be enhanced over the thermal case. It is, therefore, interesting to study in more detail the effect of light illumination on the crystallization behaviour of chalcogenide glasses.

The present paper reports the effect of light illumination on the crystallization kinetics in a-$Se_{80-x}Te_{20}In_x$ ($0 \leqslant x \leqslant 10$). The results indicate that light illumination enhances the crystallization effect since the total time, for the amorphous to crystalline transformation, at a particular temperature, decreases on exposure to light. Section 2 describes the experimental details. The results obtained in this work are discussed in section 3. The final section discusses the conclusions drawn from the present work.

2. Experimental details

Bulk $Se_{80-x}Te_{20}In_x$ ($0 \leqslant x \leqslant 10$) specimens were prepared as glasses by continuously heating the constituents at 600 °C for 10 h inside evacuated (1.333×10^{-3} Pa) quartz tubes (length ~5 cm and diameter ~8 mm) that were finally quenched in iced water. The glassy nature of the samples was verified using X-ray diffraction.

Thin films of these alloys were prepared by vacuum evaporation, the substrate was maintained at room temperature at a base pressure of about 1.3 mPa. Predeposited thick In electrodes on well degassed glass substrates were used for electrical contact. The amorphous films were kept inside the deposition chamber for about 24 h to allow thermodynamical equilibrium to be obtained, an important step in the preparation of chalcogenide glasses, as stressed by Abkowitz *et al.* [10].

In order to study the crystallization kinetics under illuminated and non-illuminated conditions, conductivity measurements have been performed in a vacuum of ~0.133 Pa on thin films that were mounted in an especially designed sample holder which has a quartz window that allows light to be shone on the films. The temperature was measured using a calibrated copper–constantan thermocouple. The annealing temperature was reached using a fast heating rate and the temperature was maintained constant until the completion of the crystallization of the sample. The sample resistance was measured using a Keithley electrometer (model 614).

The crystallization was monitored by measuring the electrical conductivity (σ) at 1 min intervals during several isothermal transformations in the range of 120–140 °C. The remarkable increase of the σ value that accompanies the amorphous to crystalline phase change implies that the measured conductivity at any annealing time is the result of two conductivities σ_a and σ_c that correspond to an amorphous and crystalline, diphasic system.

3. Results and discussion

3.1 Electrical conductivity measurements

The use of conductivity measurements to characterize the volume fraction which has crystallized (α) depends on the specific regimes of partial transformation. Figs 1 and 2 show the time dependence of the electrical conductivity (σ) of a $Se_{75}Te_{20}In_5$ sample measured at three temperatures in the range 120–140 °C under purely thermal as well as under illuminated conditions. Fig. 3(a and b) illustrates the variation of the conductivity and α as a function of time for an a-$Se_{75}Te_{20}In_5$ film, annealed at 120 °C in the dark and with photo illumination.

During the transformation process, there appears to be three regimes in a σ versus annealing time plot. The

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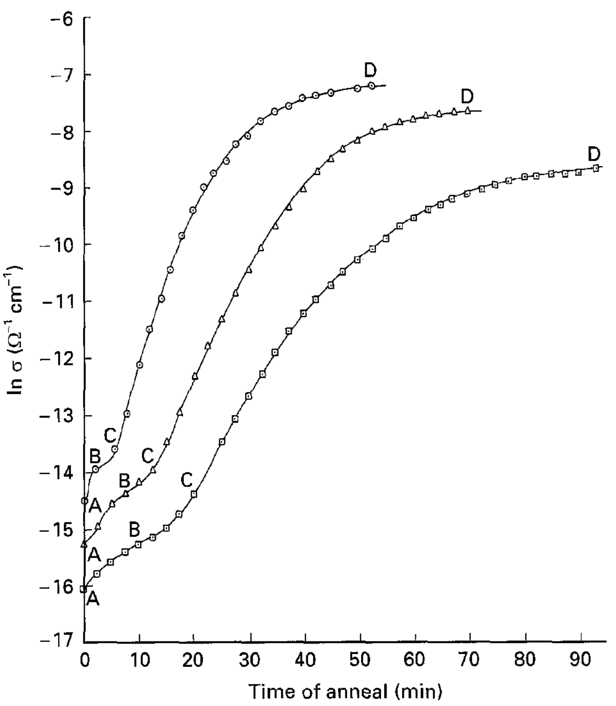

Figure 1 Time dependence of conductivity during crystallization of a-$Se_{75}Te_{20}In_5$ without illumination at temperatures of (□) 120 °C, (△) 130 °C and (○) 140 °C.

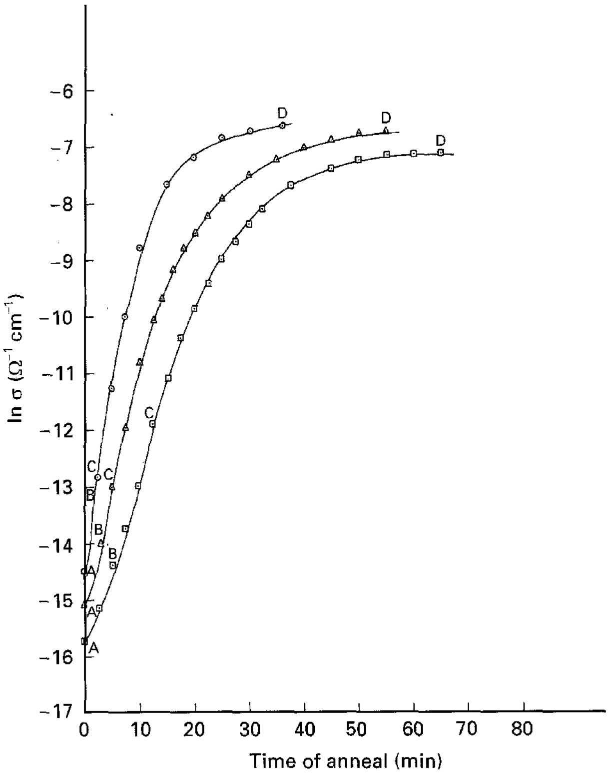

Figure 2 Time dependence of conductivity during crystallization of a-$Se_{75}Te_{20}In_5$ under illumination at temperatures of (□) 120 °C, (△) 130 °C and (○) 140 °C.

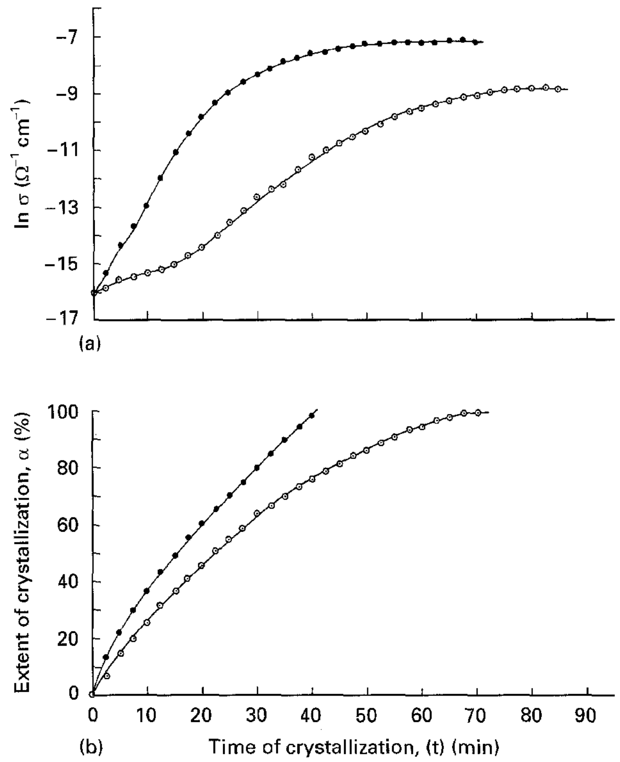

Figure 3(a) Time dependence of conductivity for a-$Se_{75}Te_{20}In_5$ crystallized at 120 °C; (●) under illumination and (○) non-illumination. (b) Time dependence of extent of crystallinity for a-$Se_{75}Te_{20}In_5$ crystallized at 120 °C; (●) under illumination and (○) non-illumination.

section AB in Figs 1 and 2 is linear and represents a gradual increase in σ as a result of the normal heating of the amorphous samples. The smaller increase in σ during the second stage, BC, is mainly accompanied by the formation of nuclei and their growth at the expense of the parent amorphous phase. The third stage, CD, which covers a relatively large increase in σ, indicates the subsequent crystal growth of the new phase until maximum crystallization of the sample volume is attained, as designated by the limiting value D, in Figs 1 and 2. In the present study we are interested in understanding the crystallization kinetics of crystal growth, i.e., part CD of the curves in Figs 1 and 2.

The total time for the amorphous to crystalline (a–c) transformation shows a decrease with increasing temperature and is lower for the measurements conducted under photo illumination for all the glassy alloys studied. Fig. 4 shows the decrease in time (Δt) with temperature. It indicates that an increase in the temperature leads to a decrease in the illumination effect on the crystallization process.

3.2 Crystallization kinetics

In order to study the kinetics of transformation, the experimental data should be expressed in terms of the transformed fraction (α) at different crystallization times (t). In the present work, $\alpha = f(t)$ is evaluated by an empirical formula suggested by El-Mously and Borisova [11] who applied it to d.c. conductivity data used as a probe in a study of crystallization kinetics.

$$\ln \sigma_t = \alpha \ln \sigma_c + (1 - \alpha) \ln \sigma_a \qquad (1)$$

where subscripts a and c refer to values at the begining and at the end of the transformation process respectively in the CD section of Figs 1 and 2. The results of $\alpha = f(t)$ at 120 °C are shown in Fig. 3(b) for $Se_{75}Te_{20}In_5$ with and without photo illumination.

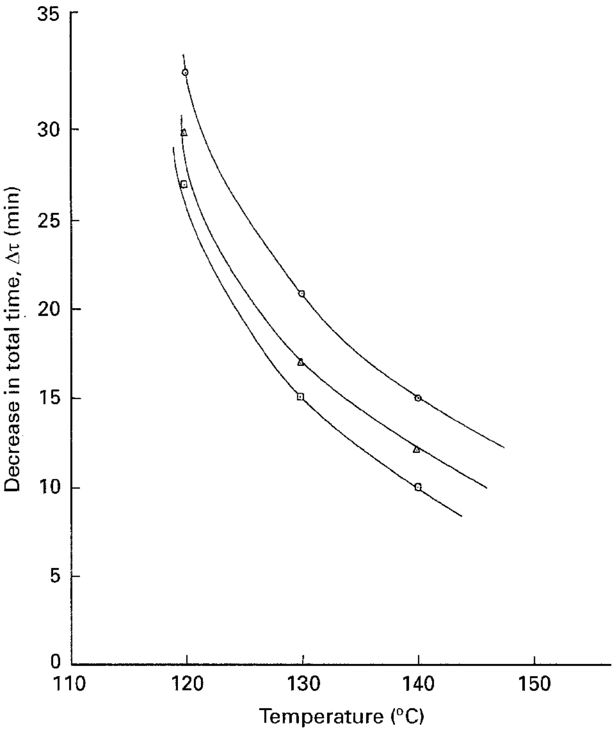

Figure 4 Temperature dependence of the decrease in total time of crystallization for; (O) Se$_{80}$Te$_{20}$, (Δ) Se$_{75}$Te$_{20}$In$_5$ and Se$_{70}$Te$_{20}$In$_{10}$.

Similar changes have been observed for each annealing temperature for all the studied glassy alloys. The crystallization during isothermal annealing has been described using the Avrami formula [12–14]

$$\ln(1-\alpha)^{-1} = \mathrm{K}t^n \qquad (2)$$

where K is the temperature dependent rate constant and n is the order parameter which depends on the nucleation and growth model [15]. To obey the Avrami equation a plot of $\ln[\ln(1-\alpha)^{-1}]$ versus $\ln t$ must yield a straight line whose slope is n and intercept is $\ln K$. Fig. 5(a and b) shows such plots for Se$_{75}$Te$_{20}$In$_5$ transformed under purely thermal conditions and with photo illumination respectively. Similar plots for other glassy alloys have been obtained. Table I lists the order parameters (n) for Se$_{80-x}$Te$_{20}$In$_x$ (x = 0, 5, 10) at different temperatures. Applying the temperature dependence of K described by the Arrhenius equation

$$K = K_0 \exp\cdot\left[-\frac{\Delta E}{kT}\right] \qquad (3)$$

where K_0 is a constant, the activation energy of crystallization (ΔE) of the samples was calculated by plotting $\ln K$ (intercepts of straight lines in Fig. 5(a and b)) versus $10^3/T$: Fig. 6(a and b) shows such plots for Se$_{80-x}$Te$_{20}$In$_x$ (x = 0, 5, 10) films for illuminated and non-illuminated cases. Table II lists the values of ΔE for all the studied glassy alloys. It has been found that there is no significant change in ΔE between dark and photo illuminated conditions. The values of ΔE in the dark closely match the published values of ΔE for the same glassy alloys in bulk form [16].

From the above results it is clear that the sole illumination effect on the crystallization behaviour is to increase the rate of crystallization thus decreasing the total time required for crystallization at a particular temperature. This may be understood as follows: when light of a certain wavelength is absorbed, a sharp increase in carrier concentration associated with the broken covalent bond occurs. These broken bonds may weaken the metastability of the amorphous state and crystallization may be enhanced at an accelerated rate. This is probably the reason why

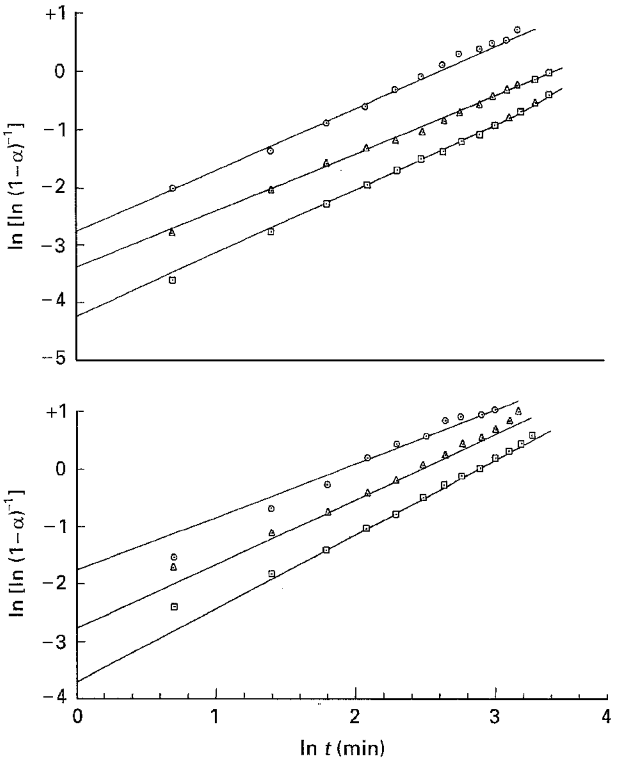

Figure 5 Avrami plots of the crystallization of Se$_{75}$Te$_{20}$In$_5$ (a) under illumination and (b) non-illumination at temperatures of (□) 120 °C, (Δ) 130 °C and (O) 140 °C.

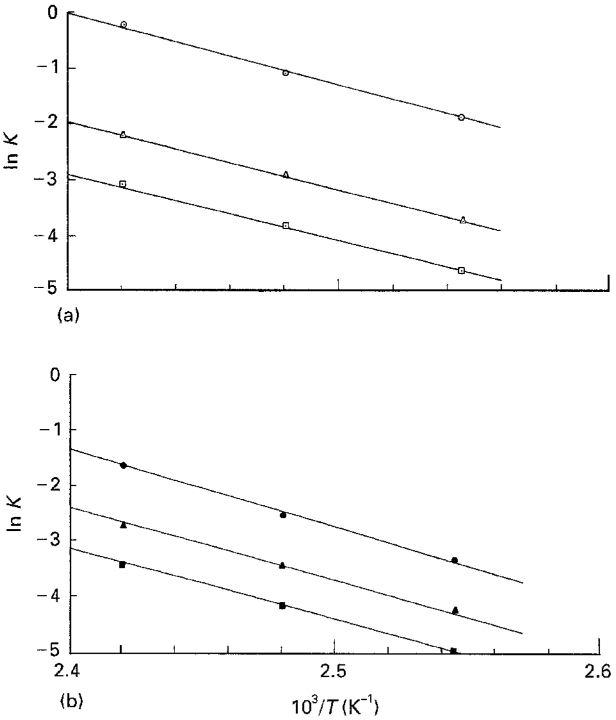

Figure 6 Arrhenius plots of crystallization under (a) non-illuminated and (b) illuminated conditions for (O) Se$_{80}$Te$_{20}$, (Δ) Se$_{75}$Te$_{20}$In$_5$ and (□) Se$_{75}$Te$_{20}$In$_{10}$.

TABLE I Temperature dependence of the order parameter (n) of amorphous $Se_{80-x}Te_{20}In_x$ films

Composition	n					
	140 °C		130 °C		120 °C	
	Non-illuminated	Illuminated	Non-illuminated	Illuminated	Non-illuminated	Illuminated
$Se_{80}Te_{20}$	0.9	1.0	1.0	1.1	1.5	1.6
$Se_{75}Te_{20}In_5$	1.1	1.0	1.0	1.3	1.1	1.4
$Se_{70}Te_{20}In_{10}$	1.0	1.2	1.1	1.3	1.1	1.2

TABLE II Activation energy of crystallization of amorphous $Se_{80-x}Te_{20}In_x$ films

Composition	Non illuminated ($kJ\,mol^{-1}$)	Illuminated ($kJ\,mol^{-1}$)
$Se_{80}Te_{20}$	116	112
$Se_{75}Te_{20}In_5$	108	104
$Se_{70}Te_{20}In_{10}$	103	100

the crystallization becomes faster in the presence of light in the present case.

4. Conclusion

The amorphous to crystalline transition (a–c) in a-$Se_{80-x}Te_{20}In_x$ ($x = 0, 5, 10$) has been studied, using electrical conductivity as a structural probe to follow the growth of crystalline phases in the dark as well as in the presence of light near the crystallization temperature. It is observed that the crystallization process becomes faster in the presence of light. The activation energy of crystallization (ΔE) and order parameter (n) have also been calculated using the Avrami theory of isothermal transformation. There is no significant change in the activation energy in illuminated conditions as compared to a purely thermal case.

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